ASETS DEFENSE
ADVANCED SURFACE ENGINEERING TECHNOLOGIES FOR SUSTAINABLE DEFENSE

ESTCP SERDP

Eliminating Cr^{6+}, Cd, and other hazardous materials without compromising performance

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Report Documentation Page

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ASETSDefense

- ASETSDefense (Advanced Surface Engineering Technologies for a Sustainable Defense) is an ESTCP initiative set up to assist DoD organizations and vendors to adopt alternatives to coatings that cause environmental and health problems
  - Defined as info source in 2009 Cr^{6+} memo
  - Information, assistance, databases
  - Workshops

DoD Vehicle Workshop

- What new regulations are coming down the road?
- What are the options to meet them?
- What works and what does not , what does it take to make new processes work well?
- What are the barriers to adopting new approaches successfully?
- What new technologies are needed, and how can existing technologies be used more effectively?

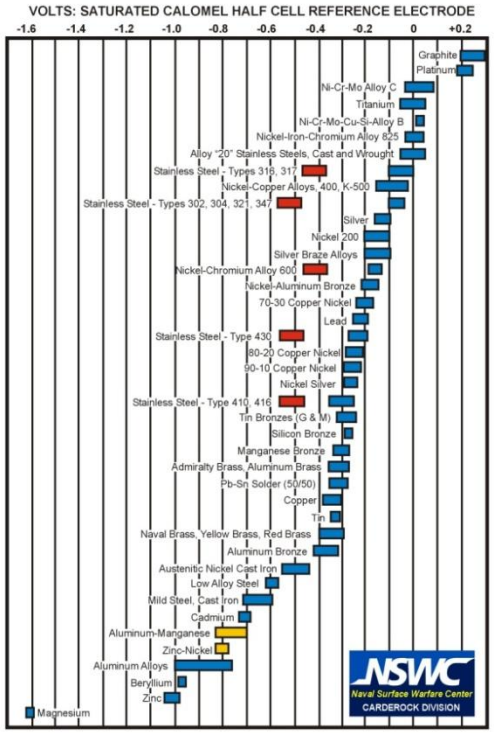
For info: www.nasf.org and www.asetsdefense.org

Weapons programs and vendors are making changes to eliminate materials such as chromates, Cd plate, VOCs. But there are more ways to do it wrong than to do it right.

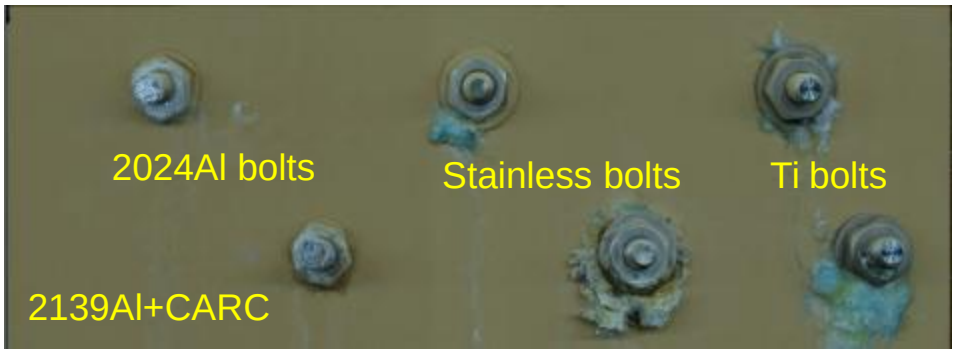
Perception is that giving up chromates etc gives up performance, but smart changes can often improve performance.

CHANGES THAT DON'T WORK OUT

Replacing Cd-plated bolts



- GTEs: most fasteners are now stainless steel
- For C-fiber composites Ti fasteners often used
- People sometimes forget that stainless steel and Ti fasteners are galvanically incompatible with Al frames and Al armor



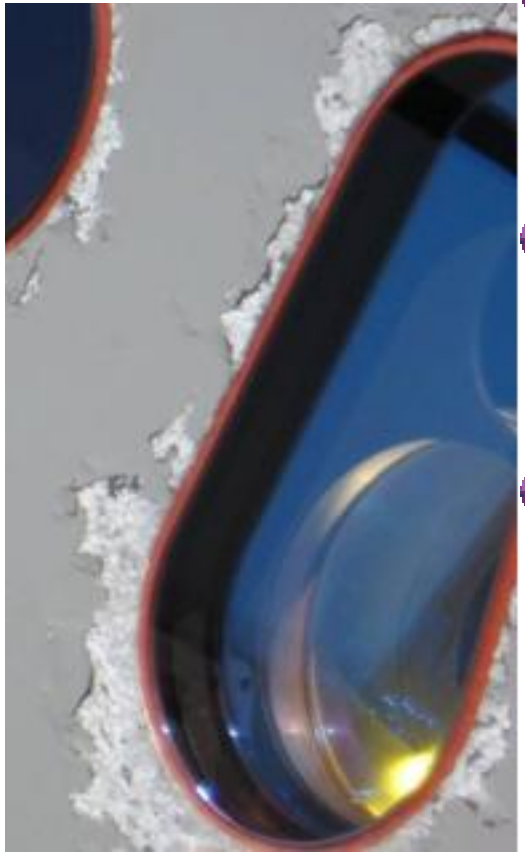
Direct-to-metal painting

- Now used on MRAPs and other vehicles to replace chromate wash
  - Some vehicles already rusting coming off the boat
    - More urgent to get vehicles in theater than to worry about initial corrosion
  - All non-chromate processes are very dependent on process conditions
  - Can be fixed on repaint

Al pretreats

- USAF has qualified Prekote in place of chromate conversion of Al aircraft skins (TO 1-1-8)
- Boeing uses AC130/131 (Boegel)
- These are both paint adhesion promoters, not corrosion inhibitors
  - Cannot be used without paint system

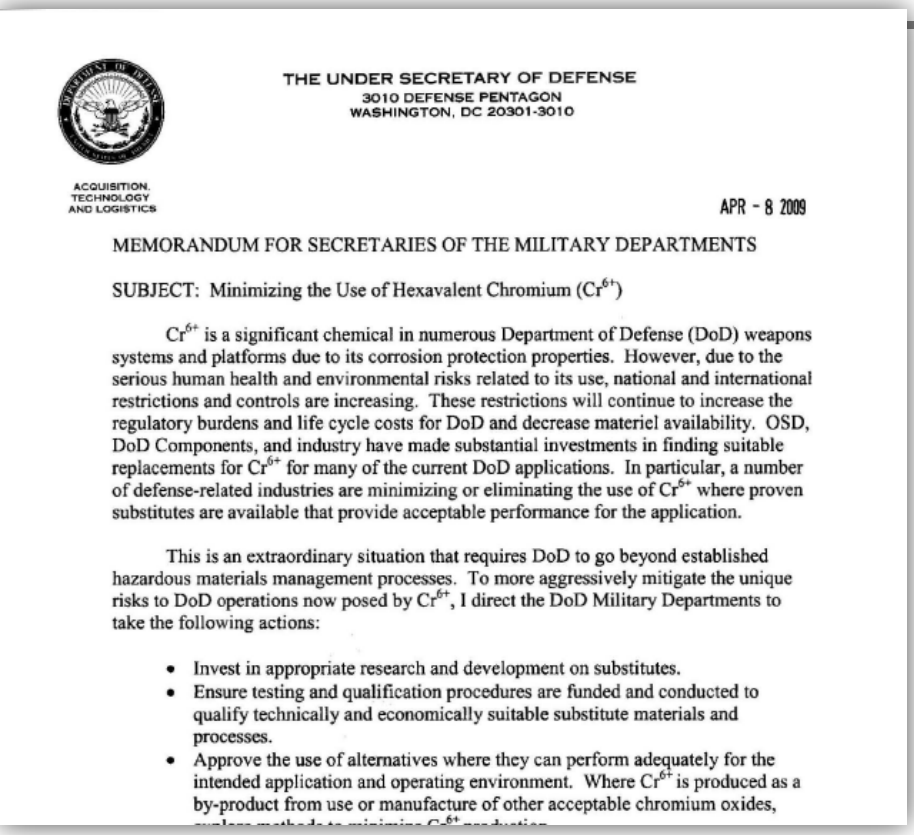
Incompatible coatings



- In order to avoid use of chromates, etc. some people are combining materials that work well alone, but not in combination
- Example: Shipboard optical sight made of Al and coated with Ni
  - Galvanic corrosion
- Electrical connectors: Updated specs such as MIL-DTL-38999L allow Al, ZnNi or electroless Ni-PTFE coatings
  - Care needed to avoid galvanic interactions

REGULATORY CLIMATE CHANGE

April 2009 DoD Memo on Cr^{6+}



THE UNDER SECRETARY OF DEFENSE
3010 DEFENSE PENTAGON
WASHINGTON, DC 20301-3010

ACQUISITION, TECHNOLOGY AND LOGISTICS

APR - 8 2009

MEMORANDUM FOR SECRETARIES OF THE MILITARY DEPARTMENTS

SUBJECT: Minimizing the Use of Hexavalent Chromium (Cr^{6+})

Cr^{6+} is a significant chemical in numerous Department of Defense (DoD) weapons systems and platforms due to its corrosion protection properties. However, due to the serious human health and environmental risks related to its use, national and international restrictions and controls are increasing. These restrictions will continue to increase the regulatory burdens and life cycle costs for DoD and decrease materiel availability. OSD, DoD Components, and industry have made substantial investments in finding suitable replacements for Cr^{6+} for many of the current DoD applications. In particular, a number of defense-related industries are minimizing or eliminating the use of Cr^{6+} where proven substitutes are available that provide acceptable performance for the application.

This is an extraordinary situation that requires DoD to go beyond established hazardous materials management processes. To more aggressively mitigate the unique risks to DoD operations now posed by Cr^{6+}, I direct the DoD Military Departments to take the following actions:

- Invest in appropriate research and development on substitutes.
- Ensure testing and qualification procedures are funded and conducted to qualify technically and economically suitable substitute materials and processes.
- Approve the use of alternatives where they can perform adequately for the intended application and operating environment. Where Cr^{6+} is produced as a by-product from use or manufacture of other acceptable chromium oxides,

- April 8 '09 USD-ATL issued memo restricting Cr^{6+} use, unless no cost-effective alternatives with satisfactory performance
- Requires Program Executive Officer (PEO) and Corrosion Control and Prevention Executive (CCPE) to certify if no acceptable alternative
- Effect will be to force adoption of Cr^{6+}-free coatings and production methods
- DFARS to be issued shortly

Info and database on Cr^{6+} alternatives available at www.asetsdefense.org

Intent of the Memo

- **Eliminate use of chromate materials and processes in <u>new</u> weapons systems unless there are no satisfactory alternatives**

"The Defense Acquisition Regulation Council will prepare a clause for defense contracts prohibiting use of Cr^{6+}containing materials in all future procurements unless specifically approved by the Government."

- **Eliminate Cr^{6+} in <u>legacy</u> systems when they are modified or overhaul methods updated**

"Application of this policy to legacy systems will be limited to modifications where alternatives can be inserted in the system modification process and updated maintenance procedures."

PEO must take manufacturability and performance into account

- **Cost-effectiveness**
- **Any change in performance**
- **Acceptable ESOH for alternative**
- **Long term availability**
- **Technical feasibility, MRL ≥ 8**
  - **Ready for at least low rate production**
    - **Stable production methods**
    - **QA/QC established**
    - **Adequate supply chain for limited production**

Cr^{6+} use can continue if alternatives not acceptable

Defense Federal Acquisition Regulation Supplement (DFARS) Modification

- **Defense Acquisition Regulation Council is drafting a Proposed Rule for the DFARS to be published in Federal Register**
- **Prohibition on Use of Cr^{6+}**
  - **DoD contracts cannot include specifications or standards requiring Cr^{6+}-containing materials or using Cr^{6+} processes**
- **Exceptions**
  - **Cr^{6+} can be used if authorized at PEO/flag level, in coordination with Corrosion Control and Prevention Executive**
  - **Does not apply to legacy systems, but alternatives to Cr^{6+} must be considered during system modifications, follow-on procurements, or updates of maintenance procedure**
- **DFARS clause would make Cr^{6+} concentrations in materials same as in RoHS**
  - **<0.1% by weight in any homogeneous material**

See ASETSDefense Workshop, Denver, September 2009

Primary EU regulations

RoHS

Reduction of Hazardous Substances

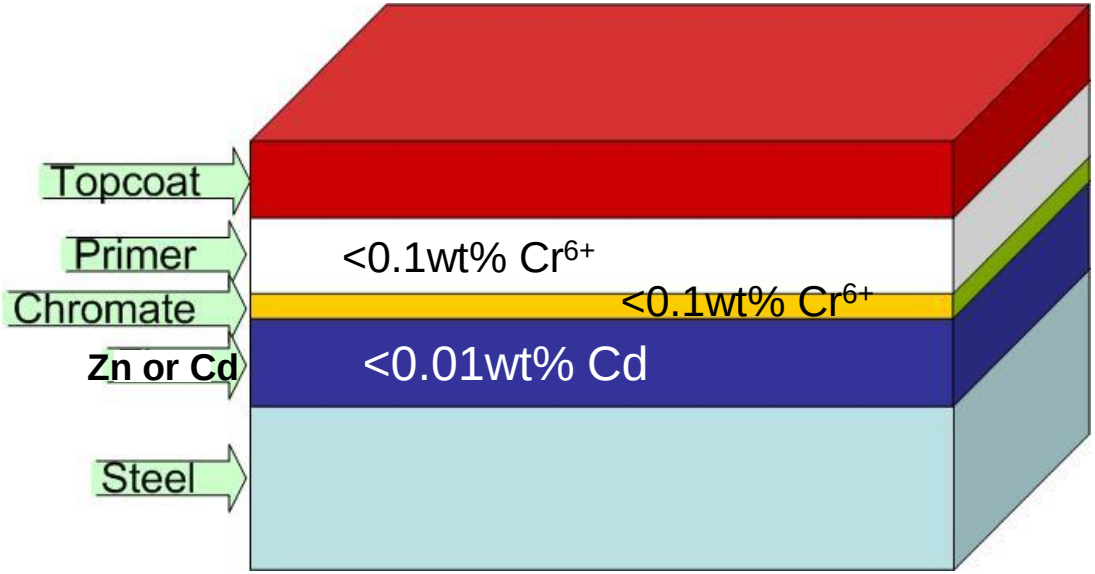
- RoHS is related to WEEE (Waste Electrical and Electronic Equipment)
- RoHS
  - Pb, Hg, Cr^{6+}, PBB, PBDE < 0.1at%
  - Cd < 0.01at%
  - Military and aerospace regarded as exempt
    - But expectation of Cd plating exemption being eliminated for all commercial products

REACH

Registration, Evaluation, Authorisation and Restriction of Chemicals

- All chemicals must be registered with EChA
  - Even if used for years
- Evaluate toxicity of everything
  - Identify SVHCs (Substances of Very High Concern) that are CMRs (Carcinogenic, Mutagenic, Reprotoxic)
- Some SVHCs may be Restricted (perhaps effectively banned)
- You must have Authorization to use other SVHCs

Obeying the rules of the RoHS



- No homogeneous layer can contain >0.1% Cr^{6+} or >0.01% Cd by weight
- "Homogeneous layer" means any layer that cannot *in principle* be mechanically disjointed
- **Not** a % of whole item. Cd is a homogeneous layer and chromate another

- Companies selling electrical equipment and vehicles in the EU must certify RoHS compliance
  - With HR 2420 we will have the same in USA
- For many organizations the biggest difficulty with meeting the RoHS requirements is with fasteners because they have no control over them
- What works depends on the environment in which they will be used

RoHS – Restriction of Hazardous Substances

- Strictly covers electrical systems and vehicles, but these days that covers almost anything
- RoHS (and its companions WEEE and ELV) have led to elimination of Cd and Cr^{6+} from cars
- Forcing consideration of alternatives to Cd and Cr^{6+} for everything else (including aircraft)
- EU discussing extending to other equipment types

- DoD and aerospace are
- Sole users of Cd plating
- Primary remaining users of Cr^{6+} conversion coatings and primers

EU Directive 67/548/EEC – Classification, Packaging and Labelling of Dangerous Substances

Seems like a simple regulation on labels for chemicals.
Is a means of bringing large numbers of chemicals under REACH restriction with minimal evidence of toxicity

- Listing a substance as CMR Cat 1 or 2 makes it potentially subject to Restriction under REACH
- New materials frequently added under "Adaptations to Technical Progress" (ATPs)
  - 30th ATP, Aug 08, added 380 new substances, reclassified 516 and removed 3
    - Added Ni sulphate, dichloride, dinitrate, and carbonate (Ni plating chemicals)
    - Boric acid (boric-sulfuric acid anodizing, alt to chromic)
  - 31st ATP, Jan 09 added 385 new substances, reclassified 83 and removed 4
    - 110 Ni compounds now included
  - New materials added by read-across, without scientific data (e.g. Ni salts)

REACH and chromates – issue for sustainment in EU

- REACH controls and restricts CMRs (carcinogenic, mutagenic, reprotoxic), defined in (Annex I of Directive 67/548/EEC, Packaging and Labeling of Dangerous Substances)
- Sodium Dichromate was put forward as a "pre-candidate substance" for inclusion in REACH Annex XIV (Authorization) in June 08
  - Decided not to prioritize for inclusion
  - ECHA intends to bring it up again by 2011
  - Listing has triggered downstream reporting requirements for Na dichromate
  - EU looking to expand to more chromates

Sodium dichromate is used in conversion coatings and to make chromic acid (used in hard chrome plating)

"…the most effective option is to group and prioritise relevant chromium VI compounds, including sodium dichromate, together" (ECHA Committee Recommendations). So it will be back, probably with all the other chromates (just as with Ni salts)

REACH impact – Impacts expected on platforms based in EU ~next 5-10 yrs

- Chromate conversion coatings, primers
  - Cr^{6+} essentially banned for all electronics by RoHS
  - Expect restriction/ authorization all chromates under REACH
- Chromated primers – need quals
  - Aircraft/vehicle repaint
- Cd plating
  - Cd on vehicles already restricted
  - Next Cd for aircraft electronics
  - Later Cd for aircraft structures
- Ni becoming serious issue
  - Big concern for wear/corrosion
- Sodium dichromate is precursor in manufacture chromic acid
  - Cr plate more difficult in EU
    - HVOF alt available
- Beryllium copper – need alts
  - Aircraft, vehicle bushings – hydraulics, landing gear
- Al-Be alloys – need alts
  - Optical, targeting systems
- Beryllium oxide – long term?
  - Heat sinks, electrical insulators – avionics
  - Small but important use

REACH Impact on DoD

Hazmat Alternatives

www.hazmat-alternatives.com

A service of Rowan Technology Group

POTENTIAL IMPACT OF EUROPEAN REACH REGULATIONS ON DOD AND MILITARY EQUIPMENT MANUFACTURERS AND SUPPLIERS

VERSION 4

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- Issue for sustainment in Europe
- Loss of local EU sources of chemicals and processes
- Uncertain whether Cd permitted for military vehicles
- Time scales for change << time scales for safe qual and adoption
- Defense Exemptions only in UK at present
  - Serious issue for ITAR (e.g. LO paint on parts made in EU)

USAGE AND REPLACEMENT – HOW MUCH DO WE KNOW?

Rule 1: There is no perfect drop-in

- Specs, approval requirements, test methods are all designed to accommodate existing processes, their strengths and weaknesses
- The only materials that ever meet the performance of Cd or Cr^{6+} in every way are Cd or Cr^{6+}
- No matter how great an alternative is there will always be one test where it is not as good
  - Is that a critical requirement?
  - Can we live with it and still do better overall?

Rule 2: Alternatives always need more care

- Everything else has a higher Coefficient of Screwupability (COSa) than Cd and Cr^{6+}
- Alternatives to chromate conversion are more process-sensitive
- If you use chrome-free primer you had better do a good job with the pretreat
- Alternative electroplates and HVOF are more difficult than hard chrome plating
- Cd alternatives: AlumiPlate requires an enclosed line, while ZnNi electroplate must have the right alloy balance all over the component

Rule 3: Alternatives always cost more up-front

- Up-front cost is almost always higher
  - Partly this is because of the extremely low cost of Cr^{6+} conversion, Cd, hard chrome, etc.
  - Partly this is because alternatives are not as widely available or used in as high volume
- However, cost of ownership (LCC) frequently lower
  - Performance often (by no means always) better
  - Lower ESOH cost (rarely >10%)
  - Lower demil and disposal cost
  - Lower liability risk for use, spills, waste disposal

Are there alternatives that improve performance?

- Replace hard chrome with HVOF WC-CoCr on hydraulic actuators, most other applications
  - HVOF WC-CoCr typically far less wear and corrosion
  - WC-Co has worse corrosion than hard chrome – not recommended
- Replace Dow and HAE on Mg alloys with Tagnite and brush Tagnite
  - Much better corrosion, damage tolerance
- Replace Cd with AlumiPlate
  - Much better corrosion resistance
- Cr^{6+}-free primer: 44GN-098 non-Cr primer less corrosion than chromated in F-35 testing

Cr^{6+} usage in DoD

Cr^{6+} (CrVI, hexavalent chrome, chromate) is our primary corrosion control material

Cr^{6+}-containing coatings

- Chromate conversion coatings
- Chromate sealers
- Chromated primers
- Chromate washes
- Chromated metallic-ceramics

Cr^{6+} processes, non-Cr^{6+} coatings

- Hard chrome plating
- Chromic acid anodizing
- Chromic acid passivation

Cr^{6+}-containing coatings are a problem for sustainment (repaint, touch-up, corrosion control)
Cr^{6+} processes are primarily a problem for OEMs and depots

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Cr^{6+}-free coatings

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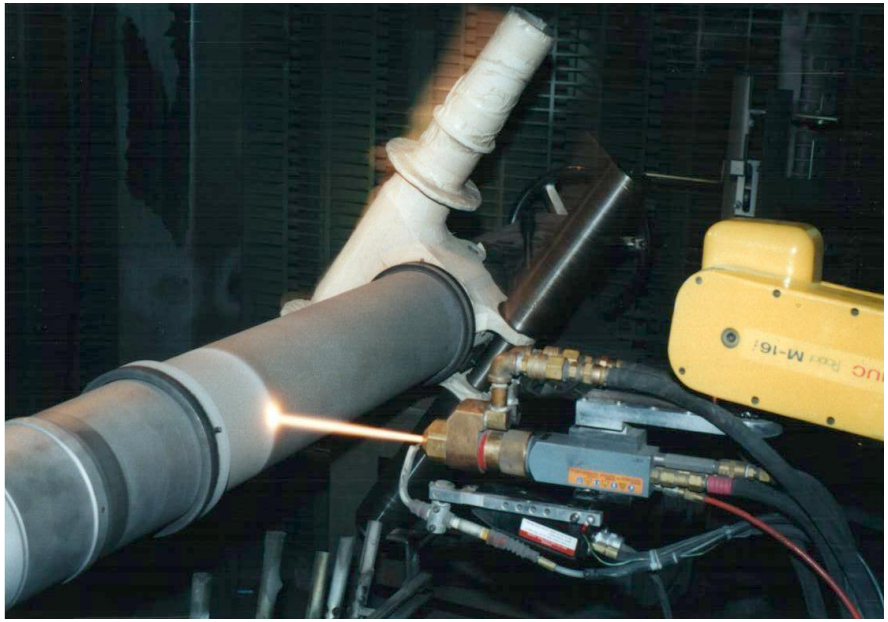
Material	Status of alternatives
Chromate conversion coating	Trivalent chrome and non-Cr commercially available. Not yet as good as Cr^{6+}. Used on cars, Boeing 777, various military systems, USAF T.O. 1-1-8 Prekote; NAVAIR TCP authorizations
Chromate primers	Non-Cr primers commercially available. Used on F-35, AH-64 Apache. Performance good on Cr^{6+} conversion coating. Moving toward total non-Cr^{6+}
Chromate finish system	Low temperature powder coat and UV curable finishes in validation to replace primer/topcoat for aircraft and vehicles. No Cr^{6+}, low VOC. In development
Chromate conversion of Mg	Tagnite now used on EFV gearbox, some sumps, gearboxes for AH-64, CH-53. Performance much better than Cr^{6+} conversion and anodize. DoD use still very limited
Metallic-ceramics	Low-Cr and non-Cr available commercially. Performance uncertain
Chromate washes	Direct-to-metal used for MRAP. Poor performance

Cr^{6+}-free processes now in use

Material	Status
Hard chrome plating	HVOF on F-35 landing gear, all new commercial and military landing gear. Being implemented for overhaul at OO-ALC.
Chromic acid anodize	TFSAA approved by NAVAIR, BSAA by Boeing
Non-Cr primer	In production on F-35, AH-64 Apache (both Cr^{6+} pretreat)

High Velocity Oxy-Fuel (HVOF) process to replace hard chrome



- Method of choice for hard chrome replacement on aircraft
  - Landing gear, actuators, flap tracks, other wear surfaces
  - Commercial off-road vehicles
  - OEM, MRO

- Most new landing gear programs now use HVOF WC-CoCr in place of hard chrome on inner cylinders, pins, actuators
  - Military and commercial aircraft
- Many hydraulics now use HVOF on actuator rods
  - E.g. Parker Aerospace
  - Caterpillar new and MRO
- Seal manufacturers specify surface finish and seal designs for HVOF
  - E.g. Greene, Tweed
- Standard industrial process
  - Several equipment makers, various powder suppliers, numerous spray houses worldwide

HVOF standard on Caterpillar off-road hydraulics, shocks

Brad Beardsley ASETSDefense Workshop 2009

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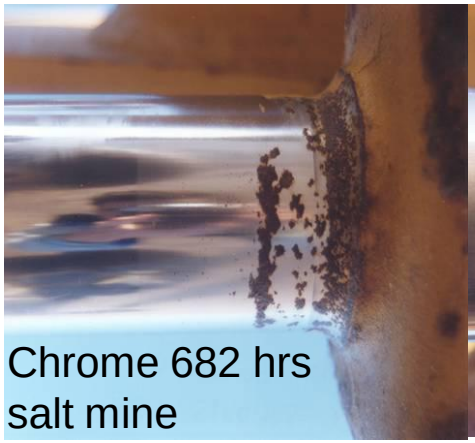
HVOF truck hydraulic production

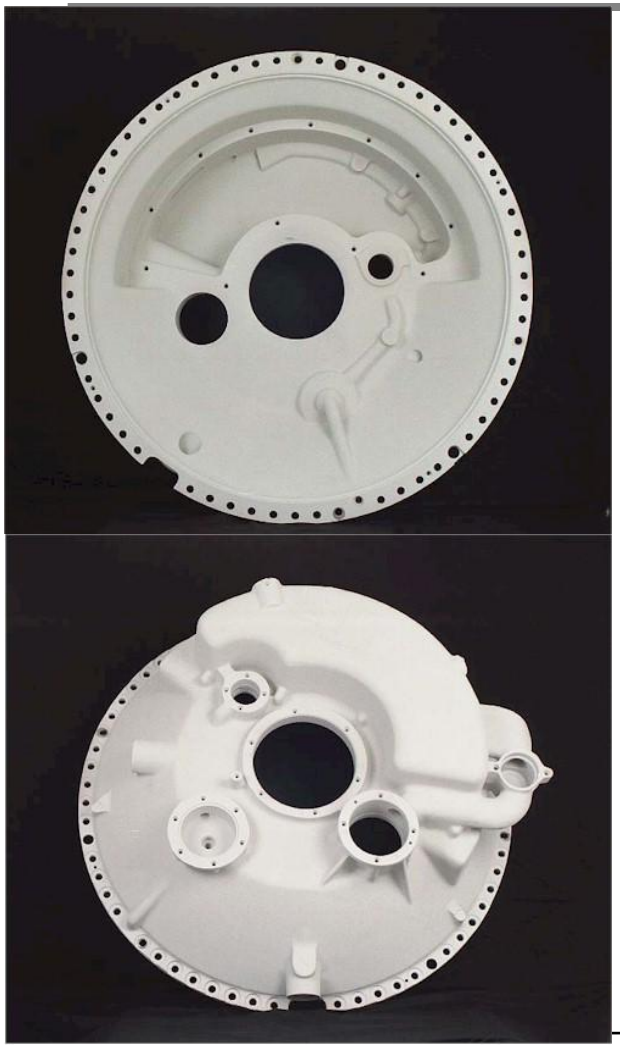
100 ton Caterpillar truck


Chrome 682 hrs salt mine


HVOF 3200 hrs salt mine


Truck strut

Tagnite to replace Dow 17 and HAE



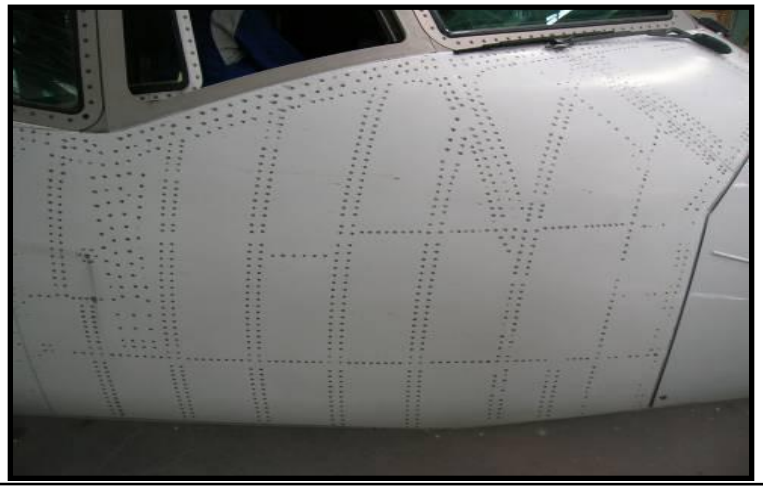
- Widely used for gearboxes in commercial helicopters
- Authorized for military helicopters but only one implementation
- EFV transmission (RR Allison)
- Much better corrosion resistance and damage tolerance than Dow or HAE
- Repair by brush Tagnite

Cr^{3+} to replace chromate conversion

- NAVAIR TCP (Tri-Chrome Pretreat) now available from QPL list of commercial suppliers
  - Works well when used correctly
  - More sensitive than chromate to prep and process
  - Currently under test as chromate wash replacement

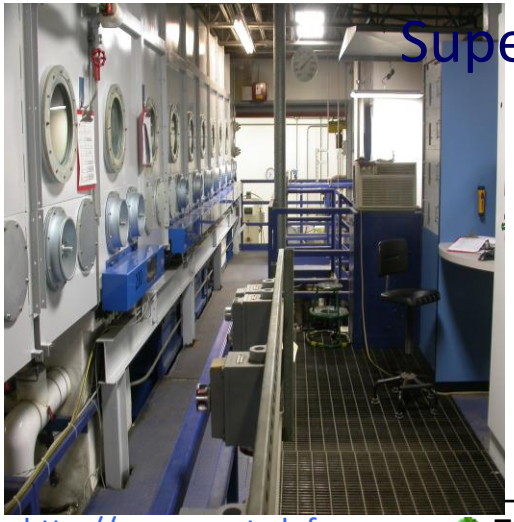
PreKote and AC-130/131 to replace chromate conversion

- USAF TO 1-1-8 specifies PreKote as chromate alternative for aircraft painting
- Boeing now uses AC-130/131 to prevent rivet rash
- Both of these are adhesion promoters not corrosion inhibitors
  - Cannot be used without paint system



AlumiPlate to replace Cd plate

- Electroplated high purity Al coating
- Has to be done in oxygen-free line
  - JCAT testing shows AlumiPlate has much better corrosion resistance than Cd
  - Much better stress corrosion cracking performance
- Used on F-35, F-22, F-16, M119 Howitzer, AH-1 Super Cobra, and other systems



F-35 MLG torque arm
Upper Cd, lower AlumiPlate

LHE ZnNi to replace LHE Cd and Ti-Cd plate

- Looks good in all Boeing testing
  - Available from Atotech and Dipsol of America
    - Not yet fully available commercially
  - ASETSDefense Workshop 09, Denver (Gaydos, Tran)
- LHE Zn14Ni currently in test at Hill AFB
  - Landing gear
- Both ZnNi and AlumiPlate require DFL
  - Usually polymer type

Al and Zn filled coatings to replace Cd on fasteners

- Ceramic or polymer base with Zn and/or Al flake fill
- Dip spin or spray
- Used on all commercial automotive fasteners
  - Several suppliers (Dorken, Delta, Magni, etc)
  - E.g. Magni 565 is modern version of Dorrltech, which tested as best TACOM testing in late 1990's
    - Inorganic Zn-rich basecoat, organic Al-rich, friction-modified topcoat
- Not good for fine threads

Powder coats and UV cure paints to replace high VOC paints

- Powder coats now formulated for low temperature cure
  - Good corrosion resistance and damage tolerance
- UV very rapid cure (seconds)
  - Saves standing around waiting for paint to dry
  - Reduces painting from days to hours
- Demonstrations of both methods ongoing

Wire arc spray to reduce corrosion – vehicles, towers, etc

- Not a direct replacement for a toxic material, but reduces environmental impact and LCC by reducing corrosion and repaint frequency
- High up-front cost, lower cost of ownership
- Wire arc Zn15Al on GSE, Patrick AFB
- Wire arc Zn, NASA towers

Problems still outstanding

- Chromate-free paint system
  - Can be done, performance not yet up to chromate
  - Cr^{3+} treatments process-sensitive
  - First chrome-free finish B-777 flying for KLM 2009
- Chromate wash for armor
  - No alternative yet that works as well as Cr^{6+} but testing under way
- Rework coatings for Mg
  - Brush Tagnite can be used on Tagnite
- Cd alternatives still in discussion
  - ZnNi or AlumiPlate

ASETSDEFENSE SOURCES OF INFORMATION

DoD Vehicle Workshop

- What new regulations are coming down the road?
- What are the options to meet them?
- What works and what does not , what does it take to make new processes work well?
- What are the barriers to adopting new approaches successfully?
- What new technologies are needed, and how can existing technologies be used more effectively?

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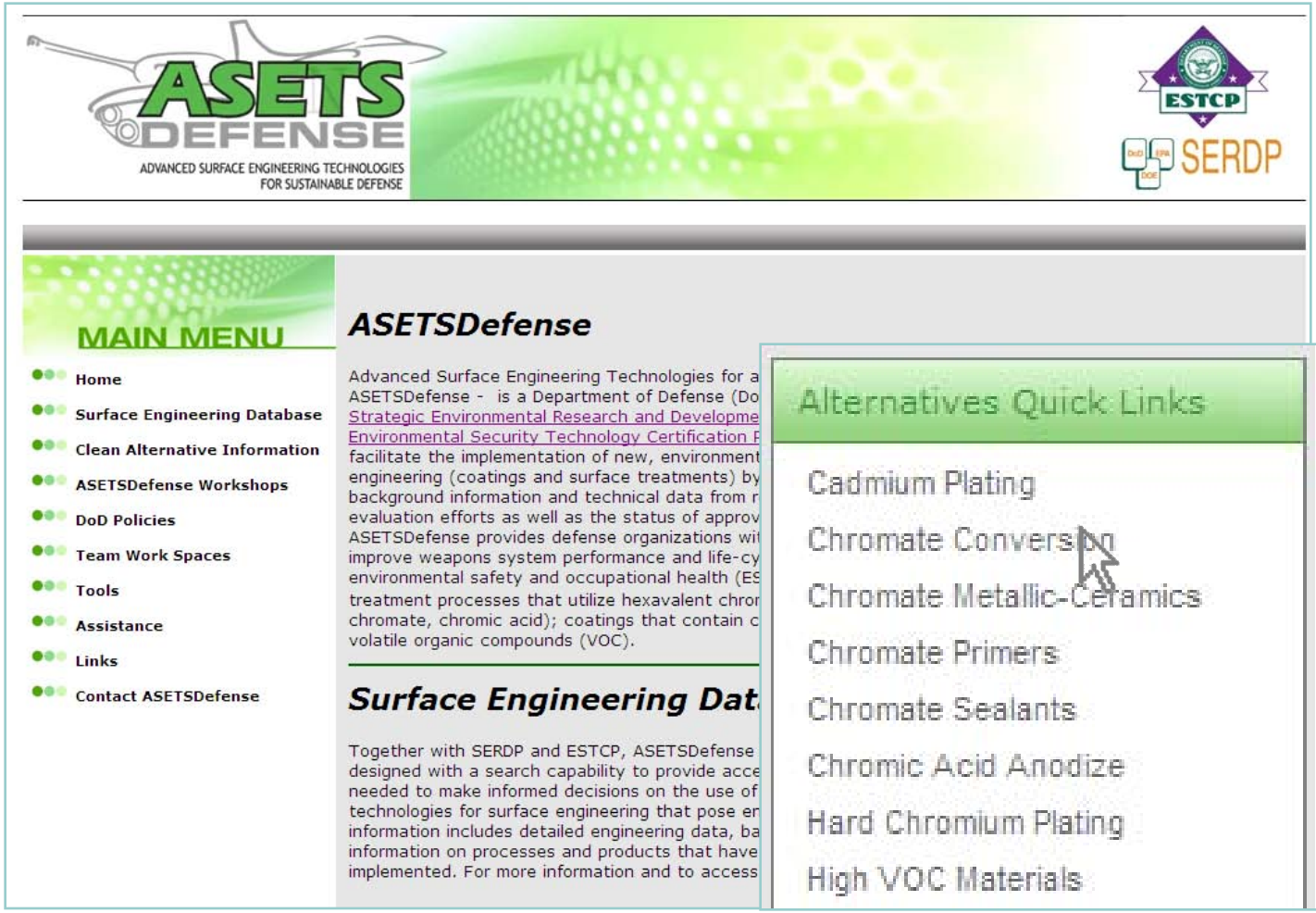

Quick information on alternatives

ASETSDefense workshop agendas, briefings, summaries (HCAT meetings coming soon)

Database

Team Work Spaces

Tools to be added

Quick Links basic information

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ESTCP SERDP

MAIN MENU

- Home
- Surface Engineering Database
- Clean Alternative Information
- ASETSDefense Workshops
- DoD Policies
- Team Work Spaces
- Tools
- Assistance
- Links
- Contact ASETSDefense

Chromate Conversion Alternatives

Current Usage

Chromate conversion coatings and chromated sealers are used to create a self-healing conversion coating on Al and Mg alloys that is resistant to corrosion. They are also used for sealing electroplated and anodized coatings. These treatments are typically used prior to painting and finishing, since they generally improve adhesion of paints and sealants.

Typical Applications	Typical Chromate Conversion Coatings	Specifications
• Aircraft skins • Al frames for aircraft and vehicles • Mg gearboxes • Corrosion-resistant coatings (Cd, Al, ZnNi, etc.) • Anodize sealing • Fasteners and electrical connectors (Zn or Cd plated) • Wash primer for steels, armor	• Conversion and sealing coatings for Al (e.g., Alodine, Iridite, etc.) • Conversion and sealing coatings for Mg (e.g., Dow 7, 17, 19, HAE anodize)	• MIL-DTL-81706 • MIL-C-5541 • MIL-M-45202 • AMS 3171 • TO 1-1-8 • MIL-A-8625 • MIL-C-3171 • MIL-C-17711 • MIL-M-45202 • DOD-P-15328 • QQ-P-416

ESOH Issues

Cr^{6+} (CrVI, hexavalent chromium) is a known carcinogen that is strongly regulated under

- EPA Clean Air Act rules
- OSHA Occupational Exposure to Hexavalent Chromium (Cr^{6+} PEL is currently $5\mu gm^{-3}$)
- European rules (RoHS, WEEE, ELV)

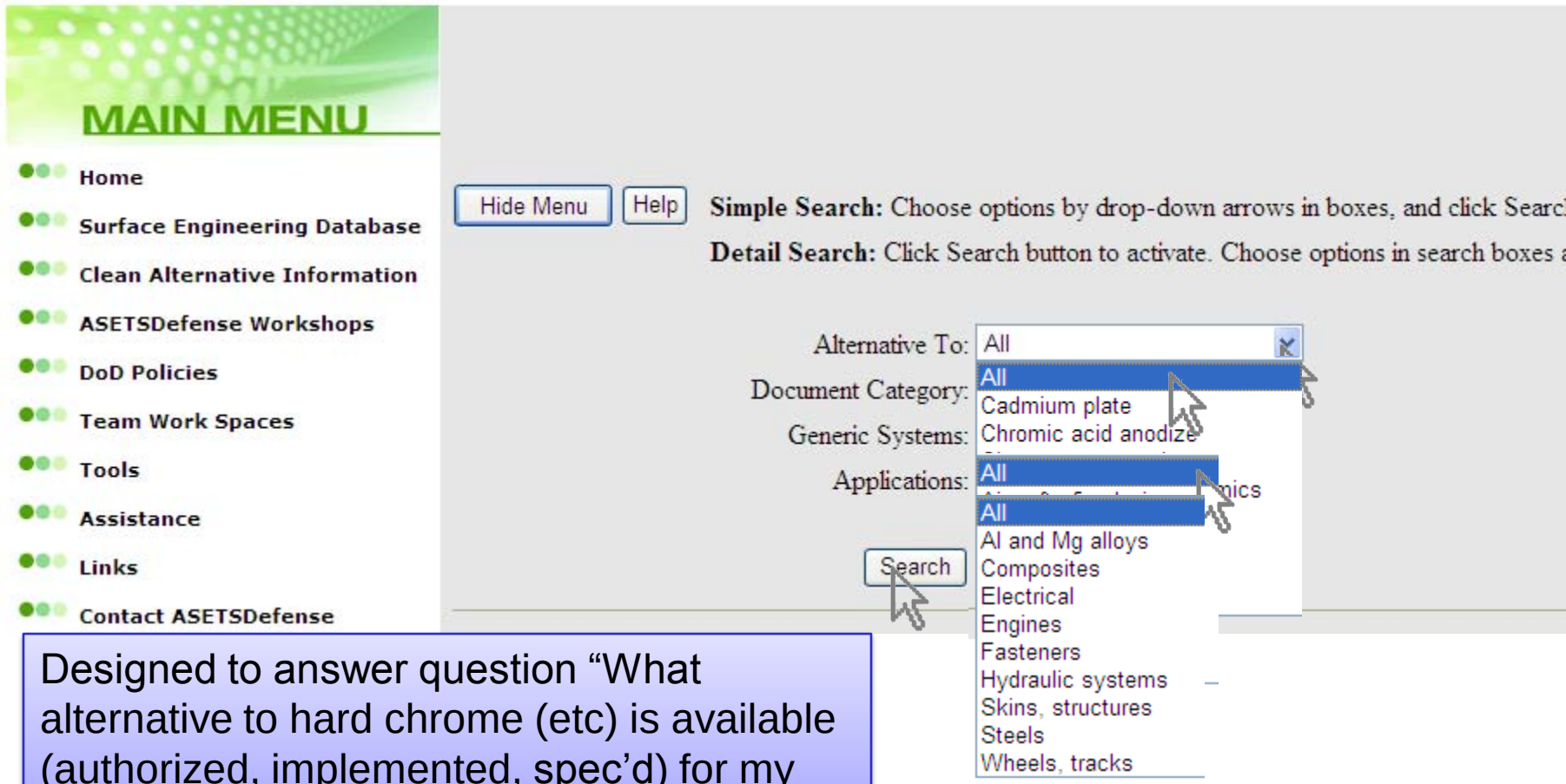
Exposure

Personnel may be exposed during manufacture, depot overhaul, repaint, and operational level touch-up and repair.

http://db.asetsdefense.org

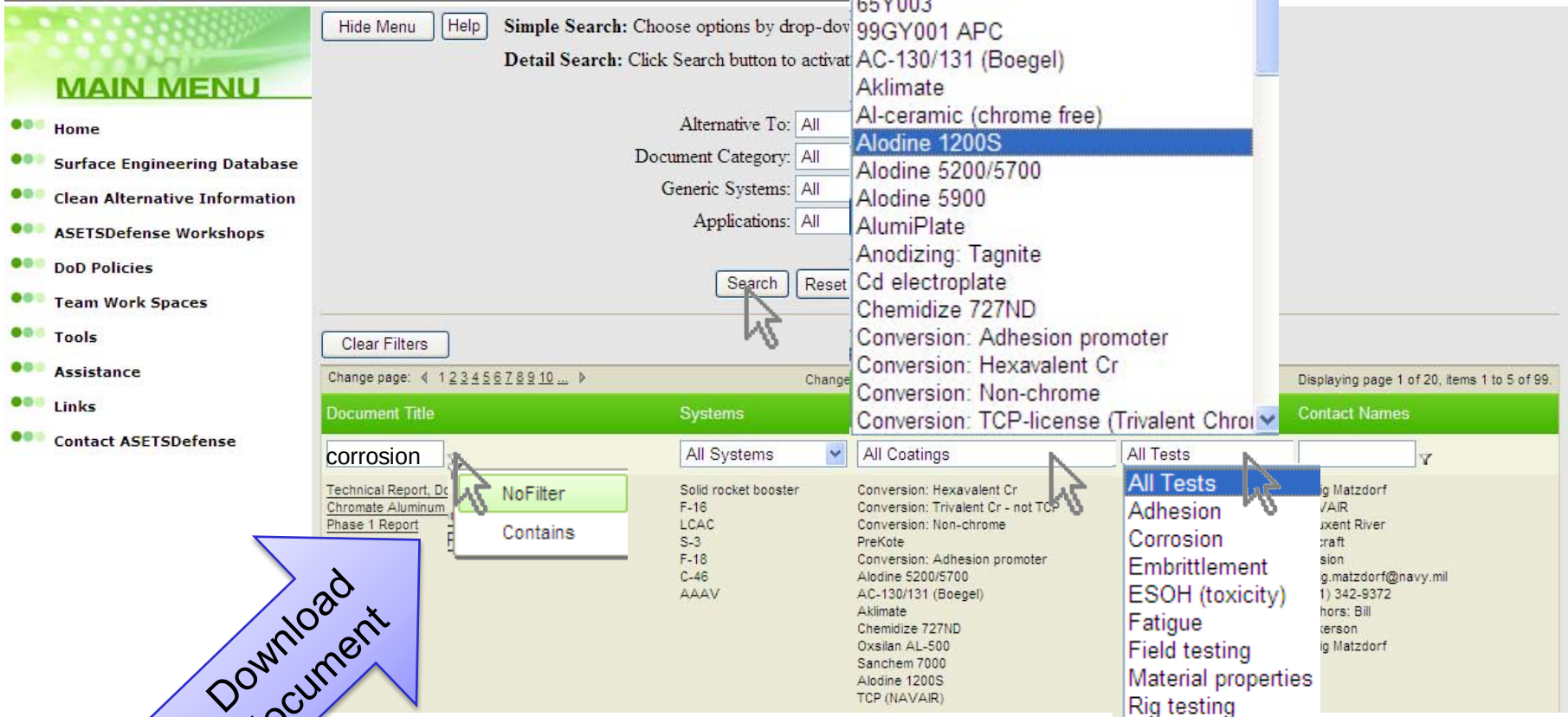
SURFACE ENGINEERING DATABASE

Database – Simple search



Designed to answer question "What alternative to hard chrome (etc) is available (authorized, implemented, spec'd) for my type of system and application?"

Detail search



Database Documents

ADVANCED SURFACE ENGINEERING TECHNOLOGIES FOR SUSTAINABLE DEFENSE

From: Commander, Naval
To: Distribution

Subj: NAVAL AIR SYST
CHROMATED PA

Ref: (a) CNASC Ltr: 131
Implementation
(b) Materials Engin
of MIL-PRF-23
Coatings, Inc.",
(c) Materials Engine
of MIL-PRF-2
Coatings
(d) Mate

Auth

1. Reference (a) authorize
Specification MIL-PRF-
paint of the existing pai
the cumulative results o

2. References (b), (c), and
Class N for Defl, Inc. (T
Product Code: 16708TE
respectively. Solventbo
must meet the same criti
85582. In addition, refe
materials. The extended
primers conforming to M
primer conforming to M
term acidified salt fog (S

3. Based on this data, NAV
the products described a
non-chromated primers
reference (a), apply to th

4. The NAVAIR points of
River, MD, phone: (301
phone: (904) 542-4516

U.S. DEPARTME
Environmental Security Tech
(EST
Joint Group on Polluti

JOINT TEST

Validation of HVOF The
Replacements for H
On Hydraulic/Pn

Test pr

ate: Augu

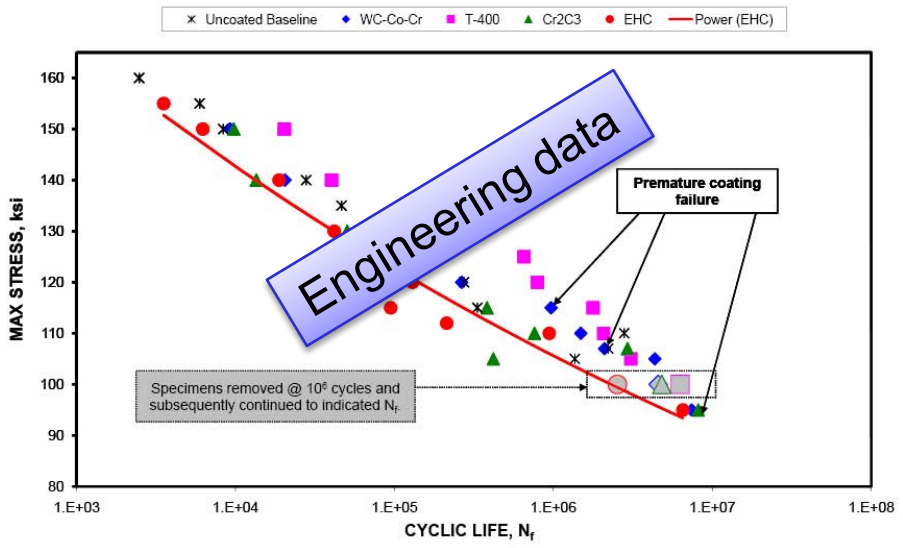
Prepar
Hard Chrome Altern

SPONSORED BY ES
HARD CHROME A

ESTCP

Fatigue and images HVOF on Actuator materials.xls

HCAT HYDRAULIC ACTUATOR FATIGUE PROGRAM
PH15-5 SUBSTRATE



Engineering data

15-5 PH Chart

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